TECHNICAL NOTE

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DETERIORATION OF CALCIA-STABILIZED ZIRCONIA

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SUMMARY

Physical breakdown and friability exhibited by fused calcia-stabilized zirconia refractories when subjected to severe cyclic heat treatment in the heat exchangers of ceramic-heated blowdown jets led to an investigation of the possible causes of deterioration. Thermal monitoring of the ceramics in the heat exchanger indicated that a definite relationship existed between time, cyclic temperature change, and deterioration of the stabilized zirconia. Slow cyclic heat treatment of zirconia ceramics in a laboratory kiln showed that continuous cycling from a temperature of $1,100^\circ$ F into the range from $1,600^\circ$ F to $2,000^\circ$ F caused physical breakdown of the stabilized zirconia material. An X-ray analysis of the crystal structure and calcia content of unused stabilized zirconia refractory and of deteriorated samples indicated that the deteriorated material was definitely less stable (contained less cubic zirconia) than unused stabilized zirconia. Deteriorated zirconia was restabilized by reheating the friable refractories to a temperature of about $3,000^\circ$ F and soaking at this temperature for at least 1 hour.

INTRODUCTION

The need for heat exchangers capable of heating air to temperatures above $3,400^\circ$ F, for use in aerodynamic and materials research at the NASA Langley Research Center, led to the construction of high-pressure heat exchangers in which fused grain calcia-stabilized zirconia was used for refractory linings and heat-storage pebble beds. Such a facility subjects the refractory material to a temperature-cycling environment, the peak cyclic temperatures for the refractory varying with location of the material in the insulating wall or pebble bed of the facility.

Operation of these facilities was successful; however, on inspection of the refractory materials after a period of operation, it was found that a severe physical breakdown of the stabilized zirconia had occurred in certain regions of the heater walls and pebble bed. A program was undertaken to determine the cause of this refractory breakdown.

Preliminary studies indicated that the breakdown was most severe in a zone that never exceeded approximately 2,100° F during operation. As this temperature range obviously did not represent a high-temperature problem for this material, it was postulated that the problem must stem from extensive crystalline inversion, characteristic of basic unstabilized zirconia, even though the calcia-stabilized zirconia used in these facilities was considered to be free of this problem. (See refs. 2 and 3.) In the production of stabilized zirconia refractory, calcia is added to the basic zirconia to form a solid-state solution, fixing the crystal structure as predominantly cubic, and producing a material reported to have good thermal shock properties and no noticeable deterioration because of crystalline inversion (refs. 1 to 3).

To substantiate the hypothesis that deteriorated zones in the heat exchanger resulted from crystalline inversion due to cycling of the partially stabilized zirconia to temperatures in the 1,600° F to 2,000° F range, an electric furnace or kiln was used to simulate the cycling temperatures to which stabilized zirconia was subjected during normal operation.

Samples taken from the deteriorated zones in the heater and from the cyclic tests in the electric furnace were analyzed and compared by means of X-ray equipment with unused partially stabilized zirconia. The degree of stabilization, and in some tests the weight percentage of calcia present, were determined to confirm the cause of deterioration and to define better the mechanism of calcia stabilization.

SYMBOLS

I_c X-ray diffraction intensity of cubic crystals

I_m X-ray diffraction intensity of monoclinic crystals

I_{Ca} X-ray diffraction intensity of calcium

I_{Zr} X-ray diffraction intensity of zirconium

2θ angle between diffracted X-ray beam and transmitted X-ray beam

MATERIALS AND TESTS

Heat-Exchanger Problem Areas

The ceramic heat exchanger (fig. 1) consists of a pressure vessel with a ceramic liner and a vertical column of ceramic pebbles used as the heat exchanging element. A single cycle or test run involves heating the pebbles and refractory liner from the top and then pressurizing the vessel and passing air through the pebble bed and attached contoured test chamber. Approximately 3 hours are required to heat the pebble bed from idling temperatures of 2,500° F

in the hot zone and 600° F at the bottom of the column of pebbles to operating temperatures of 4,000° F in the hot zone and 1,000° F at the bottom of the column of pebbles. The blowdown portion of the cycle takes approximately 5 minutes.

Deterioration, or physical breakdown of the refractory brick to a crumbled powder or friable state, occurred within a narrow annular band 1 or 2 inches wide in the heat-exchanger lining at various depths. The deteriorated refractory material represented by the heavy line in figure 2 and deformed pebbles located in the zone where the line emerged to the hot face of the liner (area B in fig. 2) were subject to cyclic heating never exceeding a maximum temperature of approximately 2,100° F. The thermal line in figure 2 was obtained by monitoring thermocouples, located in various positions in the ceramic liner, during normal operation.

Materials

The material studied in this investigation was fused partially stabilized zirconia which in the unused form has the following composition:

Compound	Formula	Percent by weight
Calcium oxide (calcia)	CaO	4.05
Silicon dioxide (silica)	SiO_2	.95
Ferric oxide	Fe_2O_3	.18
Titanium dioxide (titania)	TiO_2	.27
Zirconium dioxide (zirconia)	ZrO_2	94.05

The grain size of this material was 14 mesh and finer, and the density was 256 to 265 pounds per cubic foot. The Ballard and Marshall process of manufacturing fused stabilized zirconia directly from ores was used in producing the material investigated. (See ref. 3.)

The curves shown in figure 3 illustrate the reason for selecting partially stabilized material for the heater installation. The crystal structure of zirconia in its basic or unstabilized form is known to change from monoclinic to tetragonal when heated and to revert back to monoclinic when cooled from temperatures above 1,600° F. A destructive volume change accompanies the change in crystal structure, or inversion, and causes the refractory material to deteriorate structurally (refs. 3 and 4). Cubic material, as shown in figure 3, has the greatest linear expansion. Partially stabilized zirconia undergoes a slight inversion, which according to the available literature does not affect stability, and has less linear expansion; therefore it is considered the best zirconia for temperature operations where refractories are subjected to thermal shock (refs. 3 and 4).

Test Procedures and Apparatus

To observe the effect of the cyclic heating experienced by stabilized zirconia in a ceramic heat exchanger, several tests were run with an electric furnace. An electric furnace was used to eliminate the possibility of a reducing atmosphere, carbon, waste gases, and the thermal shock that may be produced when firing by gas. Cyclic heating between $1,100^\circ$ F and $2,000^\circ$ F or $2,100^\circ$ F and various heating rates were incorporated into the furnace operation through program controls located in a Brown recorder used to collect thermal data from the furnace. A photograph of the test setup is shown in figure 4. To insure that the only stresses on the samples in the furnace were those resulting from temperature and cycling, no compressive loads were placed on the sample. The furnace was kept closed during the entire operation, and a slow heating and cooling schedule was followed to decrease the possibility of deterioration due to thermal shock. The temperature range and heating rates were controlled to insure that all segments of the samples were heated to temperatures between $1,600^\circ$ F and $2,000^\circ$ F, and then cooled to below $1,500^\circ$ F.

One-inch cubes cut from an unused brick and 3/8-inch pebbles were fired in the electric furnace for 41 continuous cycles between $1,100^\circ$ F and $2,100^\circ$ F. One cycle took approximately 5 hours. The samples were heated at 12.5° F per minute and cooled at 5° F per minute. Idling temperatures experienced by the refractories in the heat exchanger were reproduced in the electric furnace by maintaining $2,100^\circ$ F in the laboratory kiln at the peak of cycle 2 for 2 hours, at the peak of cycle 6 for 31 hours and 20 minutes, and at the peak of cycle 40 for 11 hours and 6 minutes.

In a second cyclic test, 1-inch cubes of stabilized zirconia were subjected to 47 continuous cycles between $1,100^\circ$ F and $2,000^\circ$ F. The samples were heated at 15° F per minute and cooled at 8.3° F per minute. One cycle took approximately 4 hours.

Deteriorated zirconia bricks and pebbles taken from critical temperature zones in the heat exchangers and samples cycled in the laboratory furnace were compared with unused zirconia. The physical strength, appearance, crystal structure, and calcia content of these samples were studied to determine whether cyclic heat treatment of stabilized zirconia in the electric furnace could produce the same changes as use in the liner of a ceramic heat exchanger. Since stabilization is dependent on the amount of calcia in solid solution with zirconia, it was necessary to determine the crystal structure and calcia content to determine how much calcia in solid solution produced a given degree of stabilization. All of the samples were ground to pass through a 200-mesh screen and examined with an X-ray diffractometer to determine the crystal structure and an X-ray spectrometer to determine the calcia content.

Completely stabilized zirconia has a 100-percent cubic crystal structure, whereas partially stabilized material contains both cubic and monoclinic crystals. The ratio of the cubic to the monoclinic phase is used as the measure of stabilization. The manufacturer supplied a graph (fig. 5) showing the relationship between the degree of stabilization and the ratio of the X-ray diffraction intensities of cubic and monoclinic zirconia.

Measures of crystalline structure were obtained by exposing samples to filtered copper X-radiation (30 kv and 10 ma) in a Phillips wide-range goniometer scanning from $2\theta = 31°$ to $2\theta = 28°$ at a speed of $1°$ per minute. The cubic peak appeared on the X-ray chart at about $30°$ and the monoclinic at $28°$, and the background was measured at $26.5°$. The intensity of each peak was measured by a fixed count technique in which the background was taken into consideration.

The procedure used to determine calcia content was similar to that used to determine crystal structure. In this operation, tungsten X-radiation (50 kv and 40 ma), a lithium fluoride crystal, and a helium atmosphere were used with the X-ray spectrometer. The calcia peak that was used appeared on the chart at about $2\theta = 113.7°$ and the zirconia at about $2\theta = 72.3°$; the backgrounds used were $2\theta = 111°$ and $71°$.

Samples of unused zirconia brick were examined with X-rays before and after leaching with dilute hydrochloric acid. The acid was used to remove all free calcia, leaving only the calcia that was in solid solution with zirconia. This procedure was used to set a standard in this investigation, to show more specifically the calcia required in solid solution with zirconia to produce a given percent stabilization. The data obtained from this X-ray analysis were correlated with information obtained by a wet chemical analysis of the same materials (performed by the manufacturer), and a calcia calibration curve was constructed (fig. 6).

The leaching process consisted of placing four 25-gram samples, taken from standard unused bricks, in diluted hydrochloric acid (50 percent concentrated hydrochloric acid and 50 percent distilled water) for 18 hours, heating the samples for 2 hours at about $190°$ F, and decanting the resulting solution from the solid.

The first deteriorated zirconia sample analyzed was friable material taken from the cold face of a brick located in the refractory liner of the hot zone (area A, fig. 2). The zirconia was graded by putting a given weight of deteriorated material on a set of sieves and screening for 1 hour. Then the material was analyzed with X-rays to investigate the variances due to grain size. The finest grain sample was leached by the method described in the preceding paragraph and analyzed to determine the state of the calcia.

The brick from which deteriorated material was obtained in the preceding investigation was cut into six sections which were used to determine by X-ray analysis the effect of the thermal gradient on crystal structure from the hot to the cold face and to observe any correlation between the crystal state and color. A second brick was taken from the $1,600°$ to $2,100°$ F zone, in the area of the refractory liner where the hot faces of the bricks were deteriorated as a check on the brick from the hot zone. This brick was cut into six sections and analyzed the same way as the brick from the hot zone.

A separate brick with a deteriorated section was analyzed with X-rays for crystal structure and calcia content before and after heat treatment at $3,000°$ F for 2 hours in a gas-fired laboratory kiln. This was done to determine the effect of heating deteriorated material above the critical temperature of $2,100°$ F.

RESULTS AND DISCUSSION

Physical Observations

The material exposed to cyclic heat in the laboratory electric furnace resembled the deteriorated material removed from the heat exchangers. One-inch cubes of stabilized zirconia, with a compressive strength of about 3,500 pounds per square inch before cycling, collapsed while being removed from the furnace (fig. 7). Three-eighths-inch zirconia pebbles cycled in the same kiln lost two-thirds of their original strength (fig. 8).

Early in the course of this investigation it was observed that in all instances zirconia refractory in the deteriorated zones of the gas-fired ceramic heat exchanger (fig. 2) had a tan or orange-red color as compared with the light orange or buff color of unused stabilized zirconia. Although the deterioration observed in the ceramic lining of the heat exchanger was reproduced in the laboratory kiln, no color change was observed.

The reason for the color change in the deteriorated material of the heat exchanger is unknown; however, material not found in the hot or deteriorated zones maintained the color of unused zirconia.

When a brick with a deteriorated face was heat treated in a gas-fired kiln at 3,000° F for 2 hours it regained the hardness and color of unused zirconia.

X-Ray Analysis

The data obtained from X-ray examination of unused zirconia before and after leaching showed that free calcia was present in the original sample (table I). These results indicate that only 3 percent of the calcia was in solid solution with zirconia to produce 80 percent stabilization, although 4 percent of calcia was present before leaching. Since the degree of stabilization remained constant, these data indicate that less calcia is necessary to produce a given degree of stabilization than has been previously reported (refs. 5 and 6).

An X-ray analysis of the graded zirconia rubbed from the friable surface of a brick taken from the hot zone of a heat exchanger indicated that 80-mesh material had approximately the same degree of stabilization and overall calcia content as unused brick. (See tables I and II.) The deteriorated zirconia that was finer than 80 mesh (more than 50 percent by weight of the sample) showed markedly less stabilization and more calcia than unused stabilized zirconia. The degree of stabilization decreased with decreasing grain size. This result suggests that the deterioration of the zirconia may have been caused by calcia coming out of solid solution. This hypothesis was substantiated by the fact that leaching the finest fraction of the deteriorated zirconia caused the percentage of calcia to drop from 4.6 to 0.5. (See table II.)

The high calcia content of the deteriorated face of the brick taken from the hot zone led to the investigation of the entire brick (fig. 9(a)). An X-ray examination of the entire brick showed a definite decrease in stabilization,

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although the percentage of calcia differed by less than 0.1 from the original calcia content. The primary purpose of this investigation was to correlate visible deterioration and color variation with change in crystal structure due to cyclic heating in a specified temperature zone. Stabilization data listed in table III indicate that the region of variation in the thermal expansion of partially stabilized zirconia may extend over a broader temperature range than the generally recognized range of 1,500° to 2,000° F shown in figure 3.

The brick shown in figure 9(b) was taken from the 1,600° to 2,100° F zone (area B, fig. 2) and analyzed for comparison with the brick taken from the hot zone. Although the two bricks were similar in appearance, the brick from the 1,600° to 2,100° F zone showed a greater degree of overall destabilization (table III). The more extensive destabilization of this brick is attributed to the fact that the local temperatures in this lower zone of the heater generally remain near the critical (1,500° to 2,100° F) range for all heater firings. Thus a wider band of deterioration is produced.

Partially stabilized zirconia cycled 41 times in an electric furnace (see section entitled "Test Procedures and Apparatus") was found to have lost approximately one-third of its stabilization.

Restabilization

To establish more firmly the effect of temperature, a zirconia brick with deteriorated zones was restabilized by heat treatment at 3,000° F for 2 hours in a gas-fired kiln. This heat treatment caused the material to regain the color and hardness of unused stabilized zirconia. The increase in the amount of cubic phase after heat treatment, as observed by use of X-ray analysis (table IV), indicated that free calcia moved into the zirconia lattice and reestablished the calcia-zirconia solid solution.

CONCLUSIONS

The results of a systematic examination of deteriorated zirconia brick from a ceramic heat exchanger indicates the following conclusions:

1. The primary reason for structural failure of stabilized zirconia in the moderate temperature zones of a heat exchanger is a loss of stabilization caused by temperature cycling to maximum temperatures in the 1,500° to 2,100° F range.

2. Loss of stabilization is brought about by the diffusion of calcia out of solid solution when the material reaches but never exceeds 1,500° to 2,100° F during cyclic operation.

3. Calcia which diffuses out of solid solution remains in the material in free form. The material can be restabilized by heat treatment to temperatures above 3,000° F.

4. Color change appears to be associated with the physical state of the material in the heat exchanger. It is a qualitative means of visibly determining areas of destabilization in gas-fired heat exchangers, although it is not necessarily a result of destabilization.

Langley Research Center,
National Aeronautics and Space Administration,
Langley Station, Hampton, Va., July 31, 1962.

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TABLE I.- PROPERTIES OF UNUSED STABILIZED ZIRCONIA BRICK

Samples	Stabilization, percent	Calcium oxide, percent by weight	Color
Unused brick	80.0	4.0	Light orange or buff
Unused brick, acid leached	80.0	3.0	Light orange or buff

TABLE II.- VARIATION IN PROPERTIES OF DETERIORATED BRICK AS A

FUNCTION OF GRAIN SIZE

Mesh	Percent of total sample by weight	Stabilization, percent	Calcia, percent	Contribution to total-sample stabilization, percent	Contribution to total-sample calcia content, percent
+80 fraction	41.6	81.5	4.1	34.0	1.7
-80+200 fraction	26.2	54.0	5.0	14.2	1.3
-200+325 fraction	13.1	21.0	8.0	2.8	1.1
-325 fraction	19.1	<5.0	4.6	1.0	.9
-325 fraction[a]	19.1	<5.0	.5		

[a]Data in this row are for same fraction as preceding row, but after leaching.

TABLE III.- PROPERTIES OF STABILIZED ZIRCONIA BRICK AFTER USE

IN THE CERAMIC HEAT EXCHANGER

Section[a]	Temperature, °F	Stabilization, percent	Calcia, percent	Color
Brick from hot zone				
1	Max., 4,000 Idle, 2,300	81.5	3.7	White
2		68.5	3.3	Whitish-tan
3		63.5	3.8	Tan
4		65.0	3.9	Tan
5		66.0	3.9	Tan
6		53.5	4.5	Tan to red-orange
[b]7	Max., 1,600 to 2,100 Idle, 1,300	51.0	5.0	Tan to red-orange
Brick from zone of 1,600° to 2,100° F				
1	Max., 1,600 to 2,100 Idle, 1,000	61.5	3.8	Orange
2		61.5	4.1	Orange
3		58.0	4.1	Tan
4		66.0	4.3	Tan
5		67.5	4.5	Light orange to buff
6	Max., 1,600 Idle, 600	70.0	4.1	Light orange to buff

[a]Sections are shown in figures 9(a) and 9(b).
[b]Section 7 is granular material removed from deteriorated face.

TABLE IV.- PROPERTIES OF DETERIORATED BRICK BEFORE AND AFTER

REHEATING TO 3,000° F

Heat-treated sample	Stabilization, percent	Calcia, percent	Color
Friable face of brick before refiring	64.0	3.9	Tan to red-orange
Friable face of refired brick (2 hr at 3,000° F)	81.5	3.9	Light orange to buff
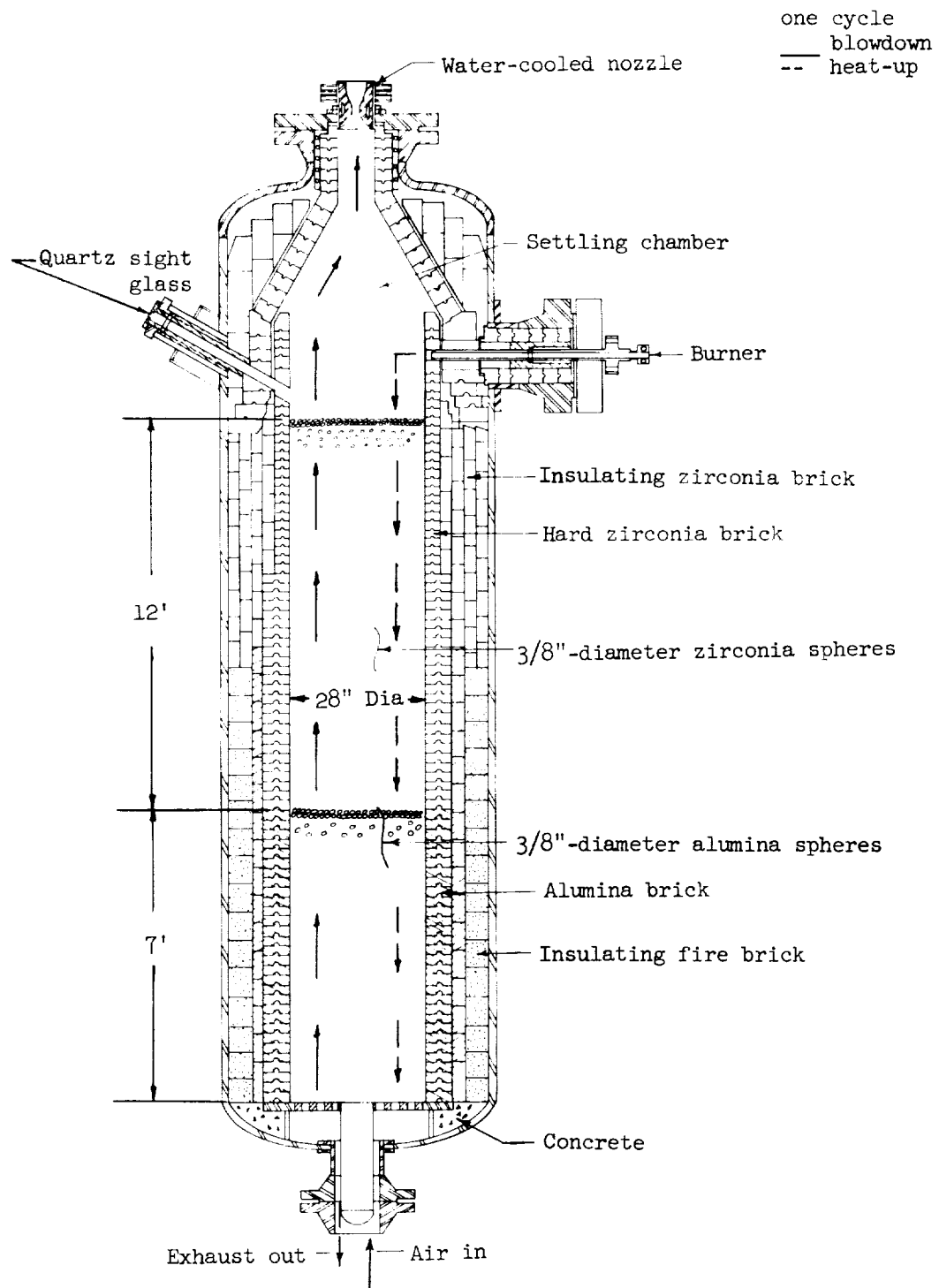
Figure 1.- Schematic drawing of ceramic heat exchanger used in the investigation.

Area A

Deteriorated or friable zone
(2,100° F max.)

Area B
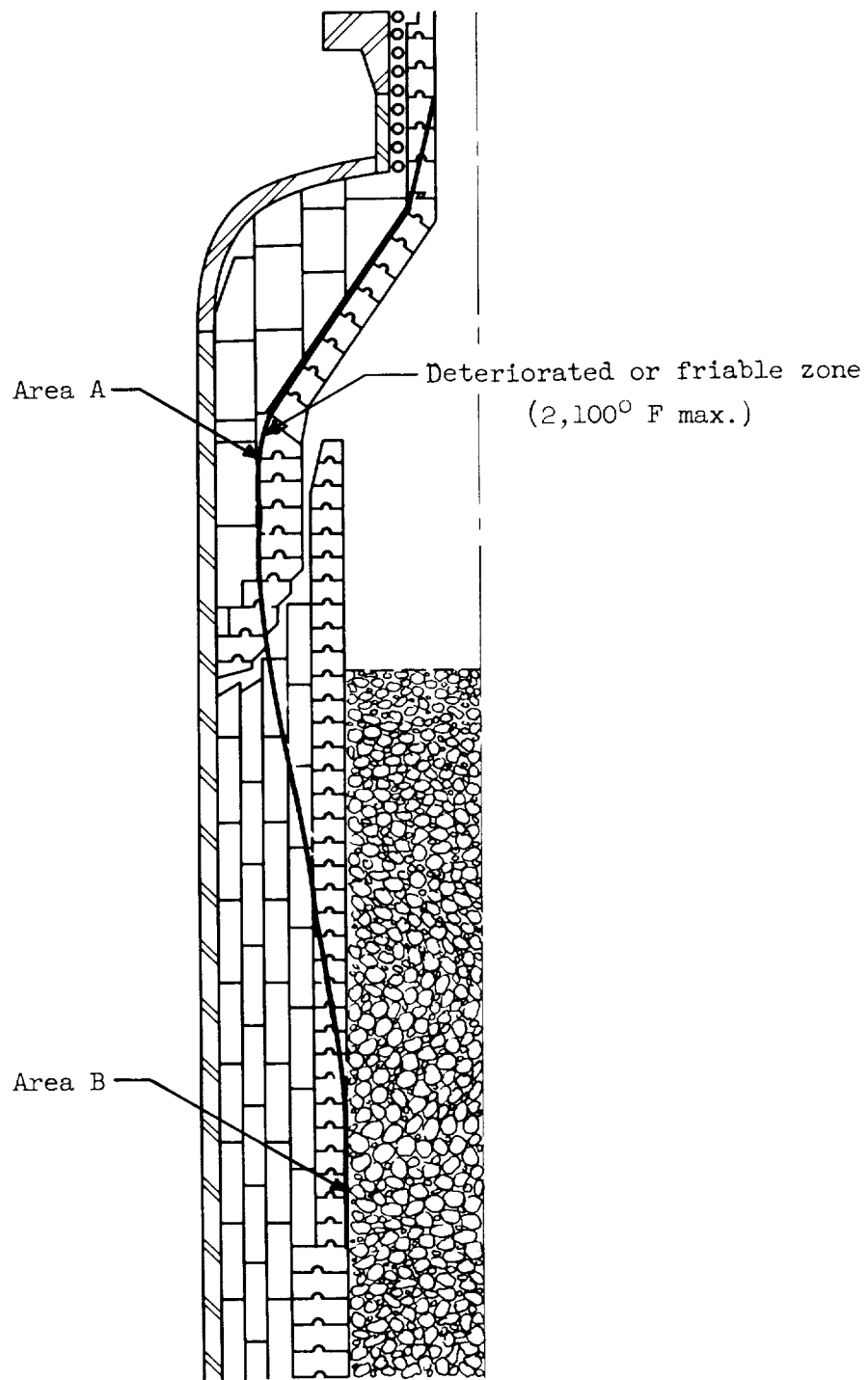
Figure 2.- Sketch showing location of zone of deterioration in the ceramic
heat exchanger.
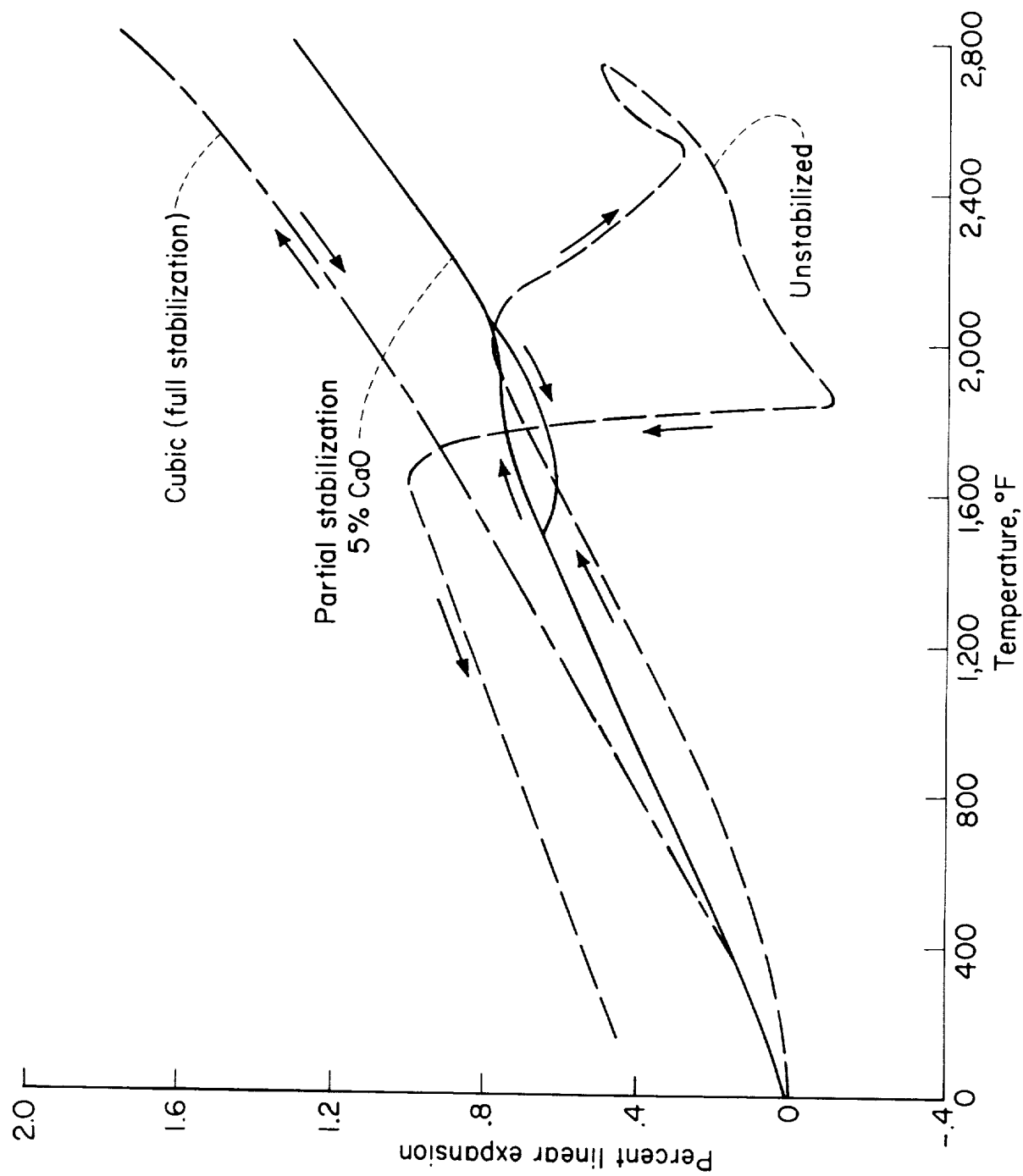
Figure 3.- Thermal expansion of zirconia having various degrees of stabilization as a function of temperature. From reference 2.

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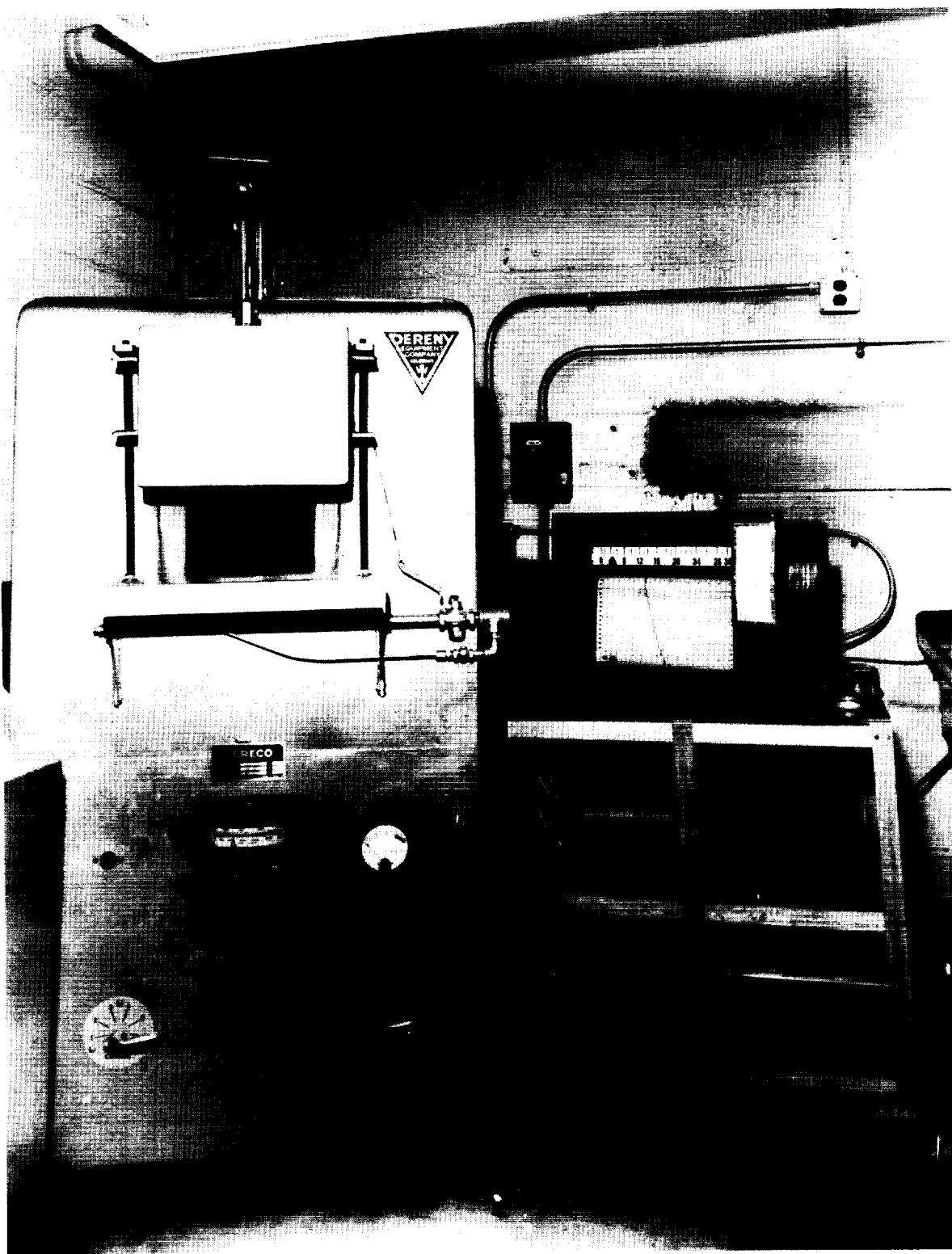
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Figure 4.- Apparatus used for temperature cycling simulation.
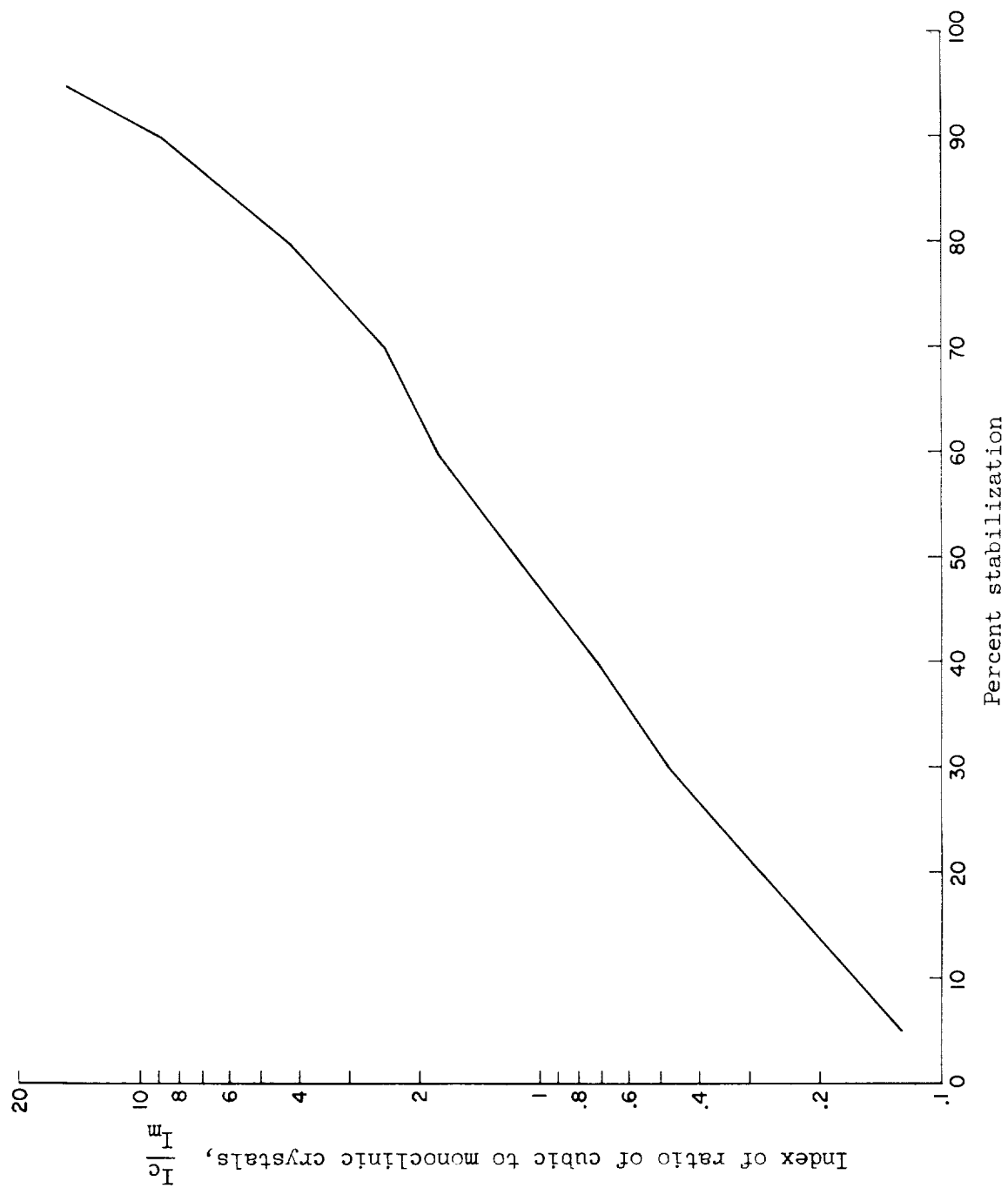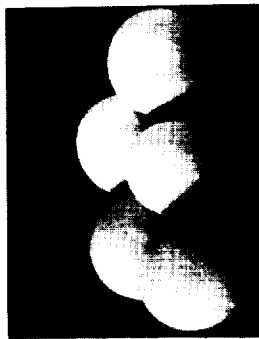
Figure 5.- Stabilization of zirconia as a function of crystalline structure.

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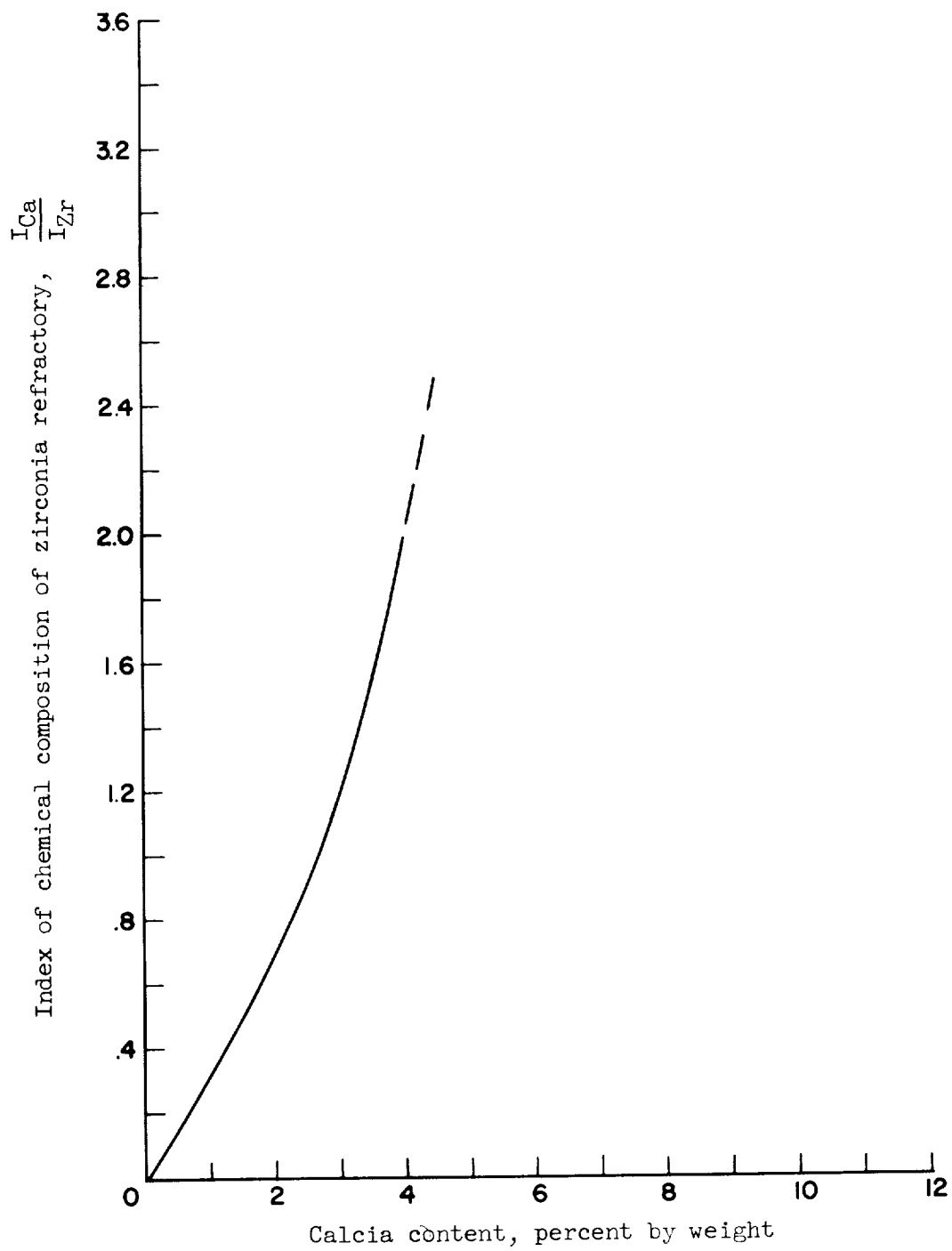
Figure 6.- Calibration curve for analysis of calcia content by
X-ray examination.

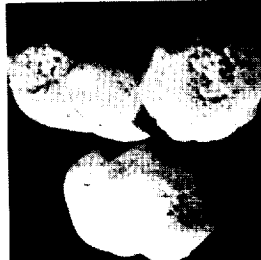Figure 7.- A one-inch cube of stabilized zirconia before and after cycling in the laboratory furnace.
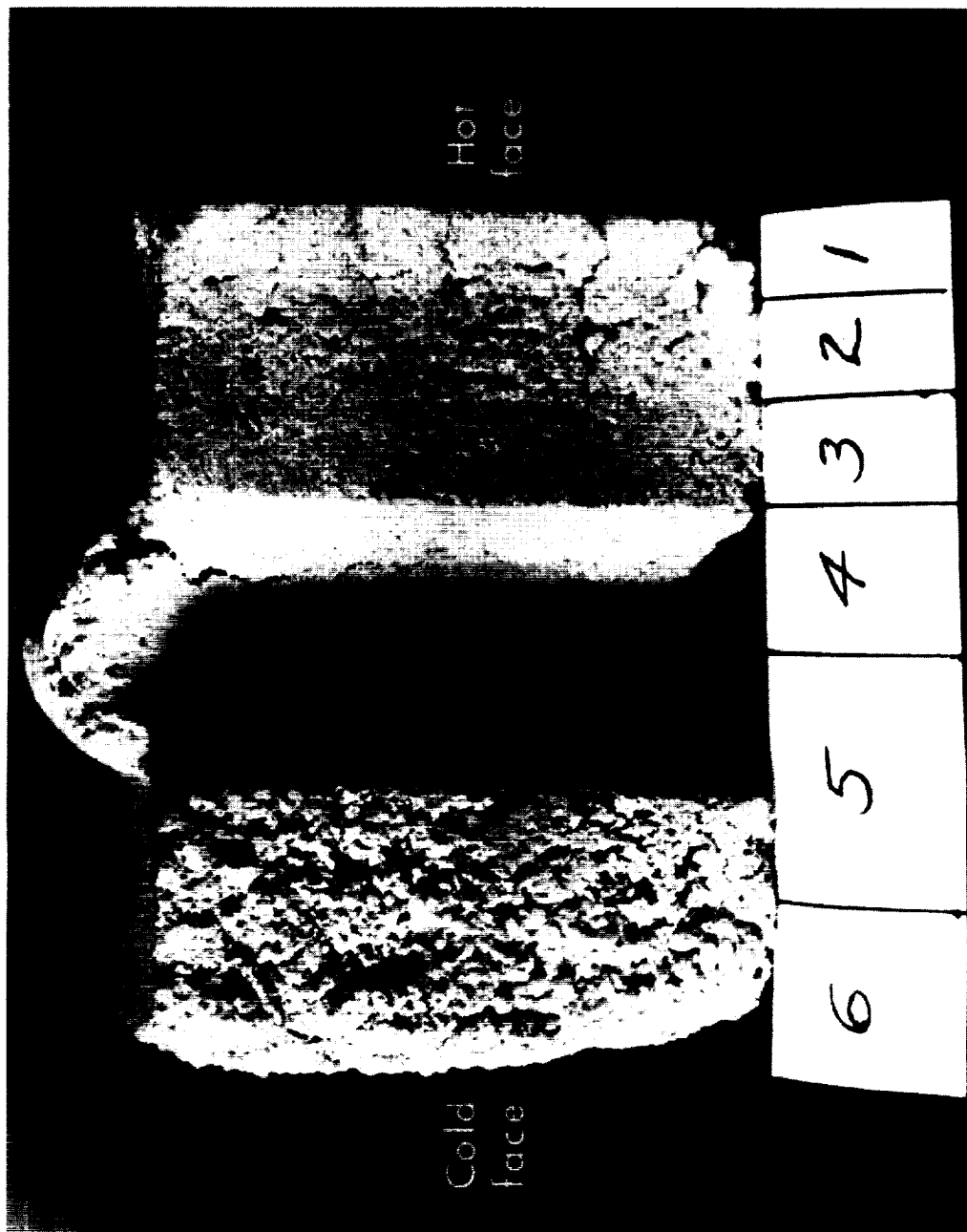
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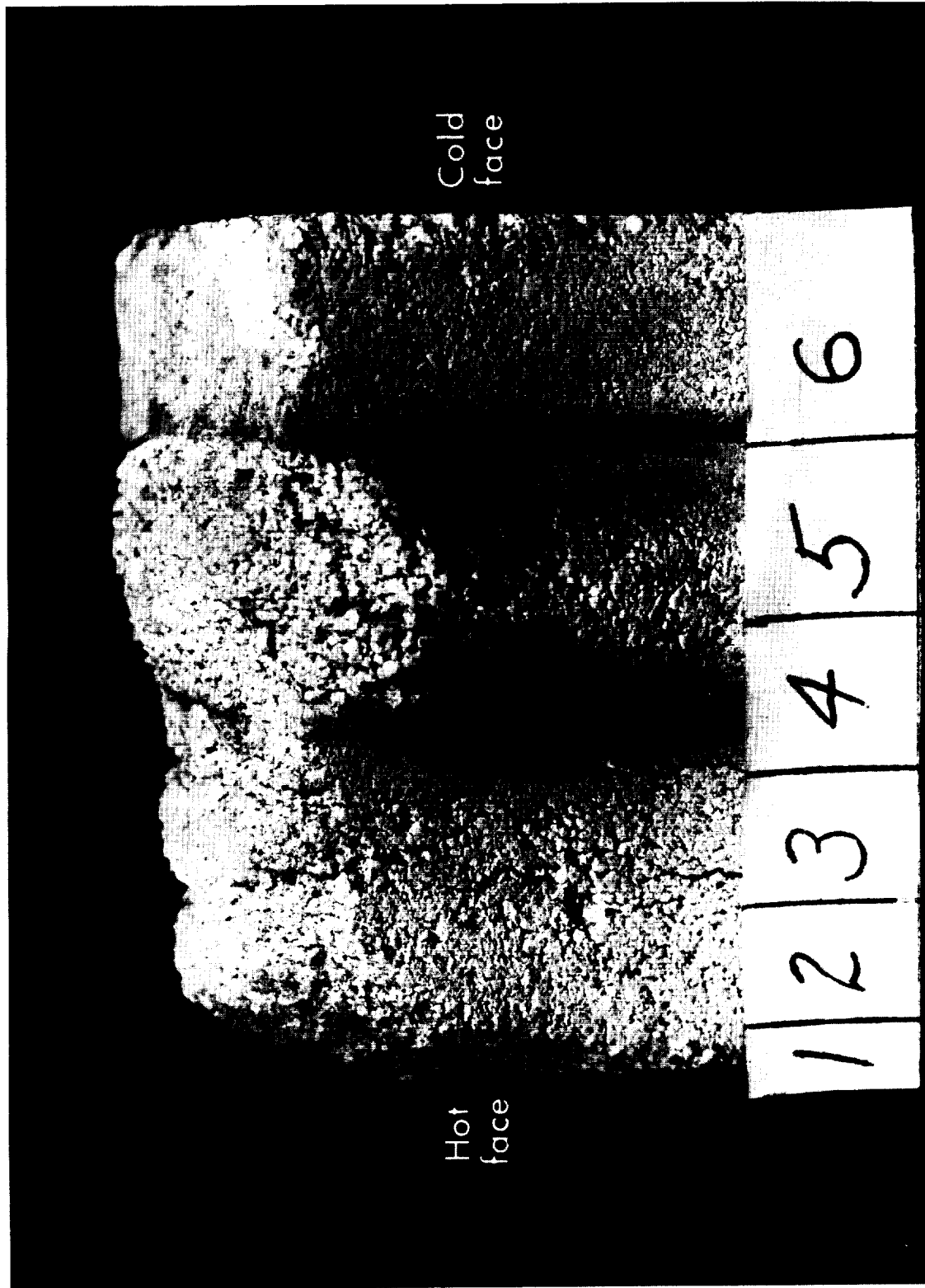
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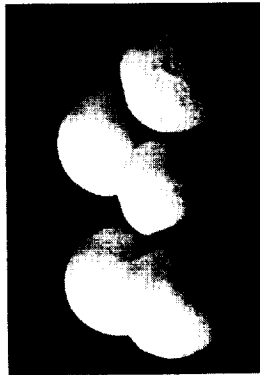
Unused   From hot zone   Deteriorated   L-62-2125

Figure 8.- Three-eighth-inch zirconia pebbles.

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(a) From hot zone (area A of fig. 2).   L-61-93

Figure 9.- Calcia-stabilized zirconia brick after use in the ceramic heat exchanger.

(b) From zone of 1,600° to 2,100° F (area B of fig. 2).   L-61-2154

Figure 9.- Concluded.